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(21) International Application Number: PCT/US99/19470 (22) International Filing Date: 26 August 1999 (26.08.99) (30) Priority Data: PCT/US98/17898 28 August 1998 (28.08.98) US 09/262,861 3 March 1999 (03.03.99) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/262,861 (CON) Filed on 3 March 2000 (03.03.00) (71) Applicant (for all designated States except US): FOSTER-MILLER, INC. [US/US]; 350 Second Avenue, Waltham, MA 02154 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): FORMATO, Richard, M. [US/US]; 13 Sean Mikeal Way, Grafton, MA 01519 (US). OSEANAR, Paul [US/US]; 100 Waltham Street #9, Watertown, MA 02472 (US). KOVAR, Robert, F. [US/US]; 203 Beach Street, Wrentham, MA 02093 (US). LANGRAU, Nelson [US/US]; P.O. Box 625, Marlborough, MA 01752 (US).		(74) Agents: BUCKLEY, Linda, M. et al.; Dike, Bronstein, Roberts & Cushman, LLP, 130 Water Street, Boston, MA 02109 (US). (81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: NOVEL ION-CONDUCTING MATERIALS SUITABLE FOR USE IN ELECTROCHEMICAL APPLICATIONS AND METHODS RELATED THERETO (57) Abstract This invention relates to novel ion-conducting materials suitable for use as solid polymer electrolyte membranes in electrochemical applications including fuel cell systems. More specifically, these novel ion-conducting polymers are based on sulfonated polyaryletherketone polymers or sulfonated polyphenylsulfone polymers, including copolymers, or blends thereof. The present invention also describes novel processes for producing these ion-conducting materials.		

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NOVEL ION-CONDUCTING MATERIALS SUITABLE FOR USE IN ELECTROCHEMICAL APPLICATIONS AND METHODS RELATED THERE TO

STATEMENT OF GOVERNMENT RIGHTS

This invention was made with Government support under Contract No. DE-FC02-97EE50478 awarded by the Department of Energy and Contract No. DMI-9760978 with National Science Foundation. The Government has certain
5 rights in this invention.

FIELD OF THE INVENTION

This invention relates to novel ion-conducting materials suitable for use as solid polymer electrolyte membranes in electrochemical applications including
10 fuel cell systems. More specifically, these novel ion-conducting polymers are based on sulfonated polyaryletherketone polymers or sulfonated polyphenylsulfone polymers, including copolymers, or blends thereof. The present invention also describes novel processes for producing these ion-conducting materials.

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BACKGROUND OF THE INVENTION

There is a considerable need in both the military and commercial sectors for quiet, efficient and lightweight power sources that have improved power density. Military applications include, but are not limited to, submersibles, surface
20 ships, portable/mobile field generating units, and low power units (i.e., battery replacements). For example, the military has a strong interest in developing low range power sources (a few watts to a few kilowatts) that can function as replacements for batteries. Commercial applications include transportation (i.e., automotive, bus, truck and railway), communications, on-site cogeneration and
25 stationary power generation.

-2-

Other interest exists for household applications, such as radios, camcorders and laptop computers. Additional interest exists in larger power sources or sources of higher power density that can be used in operating clean, efficient vehicles. In general, there is a need for quiet, efficient, and lightweight power sources anywhere stationary power generation is needed.

Additionally, the use of gasoline-powered internal combustion engines has created several environmental exhaust gas-related problems. One possible solution to these environmental problems is the use of fuel cells. Fuel cells are highly efficient electrochemical energy conversion devices that directly convert the chemical energy derived from renewable fuel into electrical energy.

Significant research and development activity has focused on the development of proton-exchange membranes for use in various electrochemical applications including fuel cell systems. Proton-exchange membrane fuel cells have a polymer electrolyte membrane disposed between a positive electrode (cathode) and a negative electrode (anode). The polymer electrolyte membrane is composed of an ion-exchange polymer (i.e., ionomer). Its role is to provide a means for ionic transport and prevent mixing of the molecular forms of the fuel and the oxidant.

Solid polymer electrolyte fuel cells (SPEFCs) are an ideal source of quiet, efficient, and lightweight power. While batteries have reactants contained within their structure which eventually are used up, fuel cells use air and hydrogen to operate continuously. Their fuel efficiency is high (45 to 50 percent), they do not produce noise, operate over a wide power range (10 watts to several hundred kilowatts), and are relatively simple to design, manufacture and operate. Further, SPEFCs currently have the highest power density of all fuel cell types. In

addition, SPEFCs do not produce any environmentally hazardous emissions such as NO_x and SO_x (typical combustion by-products).

The traditional SPEFC contains a solid polymer ion-exchange membrane that lies between two gas diffusion electrodes, an anode and a cathode, each commonly containing a metal catalyst supported by an electrically conductive material. The gas diffusion electrodes are exposed to the respective reactant gases, the reductant gas and the oxidant gas. An electrochemical reaction occurs at each of the two junctions (three phase boundaries) where one of the electrodes, electrolyte polymer membrane and reactant gas interface.

During fuel cell operation, hydrogen permeates through the anode and interacts with the metal catalyst, producing electrons and protons. The electrons are conducted via an electrically conductive material through an external circuit to the cathode, while the protons are simultaneously transferred via an ionic route through the polymer electrolyte membrane to the cathode. Oxygen permeates to the catalyst sites of the cathode, where it gains electrons and reacts with protons to form water. Consequently, the products of the SPEFC's reactions are water, electricity and heat. In the SPEFC, current is conducted simultaneously through ionic and electronic routes. Efficiency of the SPEFC is largely dependent on its ability to minimize both ionic and electronic resistivity to these currents.

Ion exchange membranes play a vital role in various electrochemical applications, including that of SPEFCs. For example, in SPEFCs, the ion-exchange membrane has two functions: (1) it acts as the electrolyte that provides ionic communication between the anode and cathode; and (2) it serves as a separator for the two reactant gases (e.g., O_2 and H_2). In other words, the ion-exchange membrane, while serving as a good proton transfer membrane, must also have low permeability for the reactant gases to avoid cross-over phenomena

that reduce performance of the fuel cell. This is especially important in fuel cell applications in which the reactant gases are under pressure and the fuel cell is operated at elevated temperatures.

5 Fuel cell reactants are classified as oxidants and reductants on the basis of their electron acceptor or electron donor characteristics. Oxidants include pure oxygen, oxygen-containing gases (e.g., air) and halogens (e.g., chlorine). Reductants include hydrogen, carbon monoxide, natural gas, methane, ethane, formaldehyde and methanol.

10

Optimized proton and water transports of the membrane and proper water management are also crucial for efficient fuel cell application. Dehydration of the membrane reduces proton conductivity, and excess water can lead to swelling of the membranes. Inefficient removal of by-product water can cause flooding of the electrodes hindering gas access. Both of these conditions lead to poor cell performance.

15

Despite their potential for many applications, SPEFCs have not yet been commercialized due to unresolved technical problems and high overall cost. One major deficiency impacting the commercialization of the SPEFC is the inherent limitations of today's leading membrane and electrode assemblies. To make the SPEFC commercially viable (especially in automotive applications), the membranes employed must operate at elevated/high temperatures ($>120^{\circ}\text{C}$) so as to provide increased power density, and limit catalyst sensitivity to fuel

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impurities. This would also allow for applications such as on-site cogeneration (high quality waste heat in addition to electrical power). Current membranes also allow excessive methanol crossover in liquid feed direct methanol fuel cells (dependent on actual operating conditions, but is typically equivalent to a current density loss of about 50 to 200 mA/cm^2 @ 0.5V). In general, fuel crossover is a

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parasitic reaction that lowers efficiency, reduces performance and generates heat in the fuel cell. It is highly desirable to minimize the rate of fuel crossover.

Several polymer electrolyte membranes have been developed over the
5 years for application as solid polymer electrolytes for use in electrochemical
oxidation reduction-driven applications, including fuel cell systems. However,
these membranes have significant limitations when applied to liquid-feed direct
methanol fuel cells and to hydrogen fuel cells. For example, the membranes in
today's most advanced SPEFCs do not possess the required combination of ionic
10 conductivity, mechanical strength, dehydration resistance, chemical stability and
fuel impermeability (e.g., methanol crossover) to operate at elevated temperatures.

DuPont developed a series of perfluorinated sulfonic acid membranes
known as Nafion® membranes. The Nafion® membrane technology is well
15 known in the art and is described in U.S. Patent Nos. 3,282,875 and 4,330,654.
Unreinforced Nafion® membranes are used almost exclusively as the ion
exchange membrane in present SPEFC applications. This membrane is fabricated
from a copolymer of tetrafluoroethylene (TFE) and a perfluorovinyl ethersulfonyl
fluoride. The vinyl ether comonomer is copolymerized with TFE to form a melt-
20 processable polymer. Once in the desired shape, the sulfonyl fluoride group is
hydrolyzed into the ionic sulfonate form.

The fluorocarbon component and the ionic groups are incompatible or
immiscible (the former is hydrophobic, the latter is hydrophilic). This causes a
25 phase separation, which leads to the formation of interconnected hydrated ionic
"clusters". The properties of these clusters determine the electrochemical
characteristics of the polymer, since protons are conducted through the membrane
as they "hop" from one ionic cluster to another. To ensure proton flow, each ionic
group needs a minimum amount of water to surround it and form a cluster. If the

ionic group concentration is too low (or hydration is insufficient) proton transfer will not occur. At higher ionic group concentrations (or increased hydration levels) proton conductivity is improved, but membrane mechanical characteristics are sacrificed.

5

As the membrane temperature is increased, the swelling forces (osmotic) become larger than the restraining forces (fluorocarbon chains). This allows the membrane to assume a more highly swollen state, but may eventually promote membrane dehydration. Peroxide radicals form more quickly as the temperature is increased; these radicals can attack and degrade the membrane. At even higher temperatures (230°C), the fluorocarbon phase melts and permits the ionic domains to "dissolve" (phase inversion of Nafion®).

10

There are several mechanisms that limit the performance of Nafion® membranes in fuel cell environments and other electrochemical applications. For example, Nafion® is sensitive to heat and can only be used effectively to temperatures of about 100°C. In fact, performance-limiting phenomenon may begin even at temperatures of about 80°C. Mechanisms which limit the performance of Nafion® include membrane dehydration, reduction of ionic conductivity, radical formation in the membrane (which can destroy the solid polymer electrolyte membrane chemically), loss of mechanical strength via softening, and increased parasitic losses through high fuel permeation.

20

Crossover problems with Nafion® membranes are especially troublesome in liquid feed direct methanol fuel cell applications, where excessive methanol transport (which reduces efficiency and power density) occurs. Methanol-crossover not only lowers fuel utilization efficiency but also adversely affects the oxygen cathode performance, significantly lowering cell performance. More

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specifically, this crossover causes a mixed reaction (oxidation and reduction) to develop on the cathode side, reducing the reaction efficiency.

5 The Nafion® membrane/electrode is also very expensive to produce, and as a result it is not (yet) commercially viable. Reducing membrane cost is crucial to the commercialization of SPEFCs. It is estimated that membrane cost must be reduced by at least an order of magnitude from the Nafion® model for SPEFCs to become commercially attractive.

10 Another type of ion-conducting membrane, Gore-Select® (commercially available from W.L. Gore), is currently being developed for fuel cell applications. Gore-Select® membranes are further detailed in a series of U.S. Patents (U.S. 5,635,041, 5,547,551 and 5,599,614).

15 Gore discloses a composite membrane consisting of a porous Teflon® film filled with a Nafion® or Nafion®-like ion-conducting solution. Although it has been reported to show high ionic conductance and greater dimensional stability than Nafion® membranes, the Teflon® and Nafion® materials selected and employed by Gore as the film substrate and the ion-exchange material, respectively, may not be appropriate for operation in high-temperature SPEFCs. 20 Teflon® undergoes extensive creep at temperatures above 80°C, and Nafion® and similar ionomers swell and soften above the same temperature. This can result in the widening of interconnected channels in the membrane and allow performance degradation, especially at elevated temperatures and pressures.

25

Further, Gore-Select®, as well as many other types of perfluorinated ion-conducting membranes (e.g., Aciplex from Asahi Chemical, Flemion® from Asahi Glass, Japan), are just as costly as Nafion®, since these membranes employ a high percentage of perfluorinated ionomers.

In an effort to reduce costs and move toward potential commercialization of SPEFCs and improved performance in all suitable electrochemical applications, ion-exchange membranes that are less expensive to produce also have been
5 investigated for use in polymer electrolyte membrane fuel cells.

Poly(trifluorostyrene) copolymers have been studied as membranes for use in polymer electrolyte membrane fuel cells. See e.g., U.S. Patent No. 5,422,411. However, these membranes are suspected to have poor mechanical and film
10 forming properties. In addition, these membranes may be expensive due to the inherent difficulties in processing fluorinated polymers.

Various sulfonated polymers have been studied for use in electrochemical applications.
15

Sulfonated polyaromatic based systems, such as those described in U.S. Patent Nos. 3,528,858 and 3,226,361, also have been investigated as membrane materials for SPEFCs. However, these materials suffer from poor chemical resistance and mechanical properties that limit their use in SPEFC applications.
20

Solid polymer membranes comprising a sulfonated poly(2,6 dimethyl 1,4 phenylene oxide) alone or blended with poly(vinylidene fluoride) also have been investigated. These membranes are disclosed in WO 97/24777. However, these membranes are known to be especially vulnerable to degradation from peroxide
25 radicals.

Sulfonated poly(aryl ether ketone) (PEK) polymers developed by Hoechst AG are described in European Patent No. 574,891 A2. These polymers can be cross-linked by primary and secondary amines. However, when used as

membranes and tested in polymer electrolyte membrane fuel cells, only modest cell performance is observed.

5 U.S. Patent No. 4,268,650 also describes sulfonated PEK polymers. The process disclosed in this patent relies on the copolymerization of PEK and polyether ether ketone (PEEK) to control the level of sulfonation in concentrated sulfuric acid. Sulfonation under these conditions is thought to occur exclusively at the ether-phenyl-ether linkages.

10 U.S. Patent No. 4,273,903 involves a similar process using polyarylethersulphone copolymers. Specifically, this patent discloses the controllable sulfonation of polyarylethersulphone polymers in concentrated sulfuric acid using copolymers of polyetherether sulfone (sulfonatable) and polyethersulfone (less susceptible to sulfonation). This patent also reports that the
15 use of sulfuric acid/oleum, oleum or chlorosulfonic acid will completely sulfonate and/or degrade the polyethersulfone polymer. The sulfonation procedure described in this reference is carried out homogeneously (i.e., putting the polymer into solution before addition of the sulfonating agent.)

20 U.S. Patent No. 5,795,496 discloses methods for producing sulfonated polyether ether ketone (PEEK) and sulfonated poly (p-phenylene ether sulfone) (PES) polymer materials for use in fuel cells. Target properties of the asymmetric membranes formed using the materials and methods of this patent include a target
25 membrane thickness of 0.05-0.5 mm (equivalent to about 2-20 mils). This patent also reports that thinner membranes, e.g., less than 0.05 mm, have poor mechanical strength and dimensional stability. This reference also describes cross-linking of these sulfonated polymer materials at temperatures of about 120°C for an unspecified time in order to minimize fuel crossover.

U.S. Patent No. 4,413,106 provides methods for the heterogeneous sulfonation (i.e., sulfonation of the precipitated polymer/solvent co-crystals) for polyarylethersulfone (PES) polymers in chlorinated hydrocarbon solvents with a sulfonating agent. This patent describes aromatic PES polymers as being

5 "notoriously difficult to sulfonate" due to the electron withdrawing effect of the sulfone linkages which deactivate the adjacent aromatic rings for electrophilic substitution. This patent further reports that sulfonation of these polymers with chlorosulfonic acid or oleum at ambient temperatures requires an enormous excess of sulfonating agent and results in a highly degraded product with the extent of

10 sulfonation being impossible to control.

This patent further reports that once easily sulfonatable PEES units are introduced to the PES polymer (PES/PEES copolymer), polymer sulfonation can be successfully controlled. PES polymers of formula (PH-SO₂-Ph-O) are known to

15 crystallize from a variety of solvents, such as CH₂Cl₂, DMF, DMAc. The crystallization is promoted by agitation or addition of non-solvents, and is highly dependent upon reaction conditions. Polymer/solvent intercrystallites (< 1 micron diameter) form as a suspension in a surplus amount of the solvent. The amount of sulfonating agent added controls the degree of sulfonation. Temperatures are

20 indicated as being preferable from -10 to 25°C.

U.S. Patent No. 5,013,765 reports the controllable sulfonation of aromatic PES polymers using sulfur trioxide (sulfonating agent) and sulfuric acid (solvent). This patent indicates that the sulfuric acid content must be less than 6% wt (based

25 upon the solvent) and that the temperature must be <30°C in order to control side reactions and degradation. Chlorosulfonic acid and oleum as sulfonating agents are discouraged since they can lead to an excessive degree of sulfonation and/or polymer degradation. Citing another source, this patent indicates that controllable sulfonation using these agents is not possible. This patent also reports that use of

-11-

sulfur trioxide in concentrated sulfuric acid can produce sulfonated polymers without by-products or degradation products, especially in the case of O-Ph-SO₂-Ph based polymers.

5 The desirability of using sulfonated poly(aryl ether) polymers in applications such as reverse osmosis has been described in the literature (D. Lloyd et al., *Synthetic Membranes: Desalination*, pp. 327-350 (1981)). This reference reports that membranes employing such polymers are highly desirable and merit further investigation. Though the chemical structure corresponding to polyphenyl
10 sulfone (PPSU) polymer is listed (among others) in this reference as being a potential candidate for sulfonation, no experimental evidence is provided on the sulfonation of PPSU.

15 Sulfonation of PPSU has been reported elsewhere (see e.g., O. Savadogo, *J. New Mat. Electrochem. Systems* 1,47-66 (1998)). However, this publication, in addition to the references cited in connection with the discussion of PPSU, are equally devoid of experimental data showing sulfonation of this particular polymer.

20 Despite the magnitude of research that has been conducted into the use of sulfonated aromatic polymers as an alternative to perfluorinated ionomers, it remains highly desirable to provide novel ion-conducting materials suitable for use in a broad range of electrochemical applications and to develop novel processes of producing such materials.

25

It also would be highly desirable to develop an improved solid polymer electrolyte membrane employing these novel ion-conducting materials. Such membranes would be suitable for use in a variety of electrochemical applications, including hydrogen or methanol fuel cell systems.

SUMMARY OF THE INVENTION

A central object of the present invention is to provide novel ion-conducting materials suitable for use in a broad range of electrochemical applications, including fuel cell systems.

In one embodiment of the present invention, these novel ion-conducting materials are based on sulfonated polyaryletherketone (PEK) homopolymers or PEK copolymers, or blends thereof. In another embodiment, these novel ion-conducting materials are based on sulfonated polyphenylsulfone (PPSU) homopolymers or PPSU copolymers, or blends thereof.

The class of PEK and PPSU homopolymers, copolymers, and blends thereof disclosed herein may include any desired substituents, provided that such substituents do not substantially impair properties desired for the intended use of the polymer, as may readily be determined by one of ordinary skill in the art. Such properties may include ionic conductivity, chemical and structural stability, swelling properties and so forth. Accordingly, as used herein, PEK and PPSU homopolymers, copolymers and blends thereof, include both substituted and unsubstituted PEK and PPSU polymers.

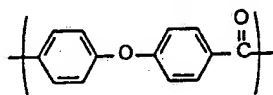
Another object of this invention is to provide novel processes for producing such ion-conducting materials.

Another object of the invention is to provide an improved solid polymer electrolyte membrane that is resistant to methanol crossover when used in a direct methanol fuel cell.

Another object of the invention is to substantially lower the overall cost of producing solid polymer electrolyte membranes to allow for commercialization of SPEFCs.

5 One preferred ion-conducting material in accordance with the present invention comprises at least one polyaryletherketone (PEK) homopolymer or at least one PEK copolymer, or blends thereof (sometimes referred to hereinafter as "PEK based ion-conducting materials"), wherein the PEK homopolymer is sulfonated and the ion-conducting material is devoid of ether-phenyl-ether
10 linkages.

In one particularly preferred embodiment of the present invention, the PEK homopolymer comprises repeating units of the formula



15 wherein the phenyl rings may be substituted or unsubstituted.

It is preferred that the PEK based ion-conducting materials have an IEC from at least about 0.5 meq./g to at least about 4 meq./g.

20

In applications where stability is important, the PEK based ion-conducting materials may further comprise sulfone crosslinkages and/or antioxidants.

The PEK based ion-conducting materials of the present invention may be
25 halogenated, e.g., brominated or chlorinated, in order to further enhance stability.

The PEK based ion-conducting materials of the present invention are useful in the preparation of solid polymer electrolyte membranes.

-14-

One preferred method of producing ion-conducting materials devoid of ether-phenyl-ether linkages suitable for use in electrochemical applications in accordance with the present invention comprises: providing a solution of at least one PEK homopolymer; adding a sulfonating agent to the PEK homopolymer solution to form a sulfonated PEK homopolymer; and isolating the sulfonated PEK homopolymer from the solution. Preferred sulfonating agents for use in this method comprise at least one of sulfur trioxide, concentrated sulfuric acid and fuming sulfuric acid. In some methods, it is preferred that the sulfonating agent has a free sulfur trioxide content of about 0 (about 100% sulfuric acid) to about 30 wt.% (about 70% sulfuric acid).

It is preferred that the PEK homopolymer solution is maintained at a reaction temperature from about 10°C to about 60°C.

One preferred method of isolating the sulfonated PEK based ion-conducting material comprises re-precipitating the sulfonated PEK homopolymer into water, water saturated with sodium chloride, methanol or other non-solvent.

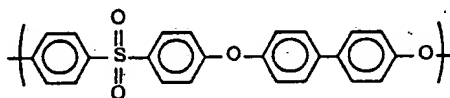
In other preferred methods, antioxidants are added to the sulfonated PEK homopolymer, either prior to or following isolation of the sulfonated PEK homopolymer. In yet another preferred method, the PEK based ion-conducting materials are crosslinked, particularly when the ion-conducting material is in the H⁺ (acid) form.

In yet another preferred method of the present invention, the PEK based ion-conducting material undergoes a halogenation step.

Another ion-conducting material in accordance with the present invention comprises at least one sulfonated polyphenylsulfone (PPSU) homopolymer or PPSU copolymer or blends thereof (sometimes referred to hereinafter as "PPSU based ion-conducting materials").

5

One preferred PPSU based ion-conducting material comprises repeating units of the formula



10 wherein the phenyl rings may be substituted or unsubstituted.

The PPSU based ion-conducting materials of the present invention have an IEC from at least about 0.5 meq./g to about 4 meq./g. In some embodiments, these materials further comprise sulfone crosslinkages and/or

15 antioxidants.

PPSU based ion-conducting materials of the present invention may be used in the preparation of solid polymer electrolyte membranes. Such solid polymer electrolyte membrane may contain sulfone crosslinkages.

20

One method of producing PPSU based ion-conducting materials of the present invention which are suitable for use in electrochemical applications comprises: providing a solution of a PPSU polymer; allowing the PPSU polymer to precipitate from the solution; adding a sulfonating agent comprising sulfur trioxide to the solution to form a sulfonated PPSU polymer, wherein the sulfur trioxide is diluted in solvent comprising a chlorinated hydrocarbon; and isolating the sulfonated PPSU polymer from the solution. Methylene chloride is one preferred chlorinated hydrocarbon solvent for use in the present invention.

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-16-

In some embodiments, the method further comprises purifying the ion-conducting material to remove overly sulfonated or degraded fractions of the PPSU based ion-conducting material. This is accomplished in one preferred method by re-dissolving the sulfonated PPSU polymer in a solvent, and re-precipitating the sulfonated PPSU polymer into water, water saturated with sodium chloride, methanol or other non-solvent.

The method of forming PPSU based ion-conducting polymers of the present invention may further comprise crosslinking the ion-conducting material, especially when the ion-conducting material is in the H^+ form.

The preferred methods may also comprise adding antioxidants to the sulfonated PPSU polymer, either before or following isolation of the sulfonated PPSU polymer. Yet other preferred methods include halogenating, e.g., chlorinating or brominating PPSU based ion-conducting materials.

The foregoing and other objects, features and advantages of the invention will become better understood with reference to the following description and appended claims.

DETAILED DESCRIPTION

The present invention relates to novel ion-conducting materials which may be used to produce solid polymer electrolyte membranes (SPEMs). These materials could also be used in composite SPEMs comprising a substrate polymer and ion-conducting material component.

The novel ion-conducting materials and SPEMs of the present invention are designed to address the present shortcomings of today's leading solid polymer

electrolyte membranes, e.g., Nafion® and other Nafion®-like membranes, such as Gore-Select®.

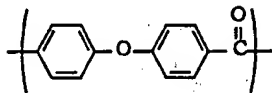
Materials and membranes of the present invention may be used in a host of
5 electrochemical applications, including but not limited to, polarity-based chemical
separations; electrolysis; fuel cells and batteries; pervaporation; reverse osmosis -
water purification, gas separation; dialysis separation; industrial electrochemistry,
such as chloralkali production and other electrochemical applications; water
splitting and subsequent recovery of acids and bases from waste water solutions;
10 use as a super acid catalyst; use as a medium in enzyme immobilization, for
example; or use as an electrode separator in conventional batteries.

Innovative processes for producing ion-conducting materials of the present
invention are also disclosed. These processes can be tailored to produce solid
15 polymer electrolyte membranes useful over a range of operating conditions and/or
applications.

Such processes generally comprise providing a solution of a
polyaryletherketone (PEK) homopolymer, PEK copolymer or blends thereof, or a
20 polyphenyl sulfone (PPSU) homopolymer, PPSU copolymer or blends thereof;
adding a sulfonating agent to the polymer solution; and isolating the sulfonated
polymer from the solution. Post-processing steps (i.e., purification, cross-linking,
use of antioxidants, chlorination or bromination of the aromatic polymer
backbone) may be employed to enhance or improve the stability of the ion-
25 conducting material and the membranes comprising these materials.

In one embodiment of the present invention, the ion-conducting material
comprises a sulfonated PEK homopolymer, PEK copolymer or a blend thereof.

One preferred PEK homopolymer has the repeating unit shown below:



5 The phenyl rings of the PEK homopolymer may be substituted or unsubstituted.

It is a feature of the claimed invention that the PEK homopolymer, PEK copolymer or blends thereof be sulfonated in the absence of ether-phenyl-ether
10 linkages (e.g., in the absence of PEK/PEEK copolymerization).

This is achieved, in part, by increasing the sulfonation power of the sulfonating solution, while preventing significant degradation of the polymer. Such innovation is in contrast to the suppositions of the prior art, e.g., that
15 aromatic groups adjacent to the protonated ketones can not be sulfonated to a useful degree.

In one preferred embodiment, PEK homopolymer, e.g., available from Victrex USA, is dissolved in concentrated sulfuric acid. Slow addition of oleum
20 reacts with the water present in the solution producing a more concentrated form of sulfuric acid solvent that eventually contains free SO₃ (after all the water has reacted). Further addition of oleum increases the sulfonating power of the solution. (The water content is lowered, thereby increasing the sulfonating power of the solution.) Care must be taken to avoid excessive SO₃ content or
25 overheating of the solution in order to minimize polymer degradation. Overhead stirring of the solution and a room temperature water bath are highly recommended.

-19-

Maintenance of the concentration of the reactant acid solution is critical. As these solutions are hygroscopic, they tend to change concentration due to moisture absorption with every exposure to air. Careful monitoring of their density can be used to check concentration. Titration may be used to monitor
5 concentration.

The sulfonated PEK based ion-conducting product can be isolated by precipitation into water provided that the extent of sulfonation has not made it water soluble (methanol / water or water saturated with salt may also provide for a
10 high degree of sulfonation). Longer reaction times or a larger excess of sulfur trioxide will cause more sulfonation.

Preferable temperature ranges for the reaction are as follows: 0-80°C including chilling the initial PEK polymer solution before, after, or during the
15 addition of the oleum. However, since pure H_2SO_4 solutions will freeze at approximately 10°C, it is preferable to maintain a temperature between 10-60°C.

Other preferred reaction conditions include using a free SO_3 content of between about 0 (about 100% sulfuric acid) to about 30 wt.% (about 70% sulfuric
20 acid). Optimal content is dependent upon other reaction conditions (i.e., temperature), but generally SO_3 content is preferred to be between 1-25wt.%.

The final concentration of polymer depends upon the starting sulfuric acid concentration, the free SO_3 level desired, and the concentration of fuming sulfuric
25 acid added. Generally preferred concentration ranges include the following:
10wt.% polymer (~5-30wt.%) in concentrated sulfuric acid (preferably 80-100%, more preferably 90-99%).

Oleum ($\text{SO}_3/\text{H}_2\text{SO}_4$) is the preferred SO_3 source for sulfonating the PEK homopolymer, PEK homopolymer, copolymer or blends thereof. A free SO_3 content is preferably between 10-60wt.%, more preferably approximately 20-30wt.%. However, pure SO_3 also may be used under the appropriate conditions.

5

The afore-mentioned reaction conditions may be tailored to produce sulfonated PEK based ion-conducting materials having IECs from at least about 0.5 to at least about 4 meq./g.

10

In accordance with the present invention, ion-conducting materials comprising sulfonated PEK homopolymers, copolymers or blends thereof, can be isolated via direct precipitation into water (or salt water) depending on the level of sulfonation.

15

Though the peroxide stability of sulfonated PEK may not be sufficient for long-term use in fuel cells, many electrochemical applications do not require hydrolytic stability at this level. For example, dialysis, electrodialysis or electrolysis systems, pervaporation or gas separation systems, or for water splitting systems for recovering acids and bases from waste water solutions, or as

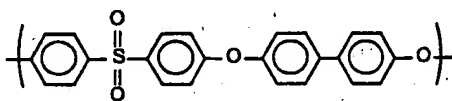
20

an electrode separator in a battery.

In another preferred embodiment of the present invention, the ion-conducting material comprises at least one of a sulfonated PPSU homopolymer, PPSU copolymer or blends thereof. This polymer has the repeating unit shown

25

below:



The phenyl rings of the PPSU polymer may be substituted or unsubstituted.

5 The prior art teaches that PEES units sulfonate readily while PES units are very difficult to sulfonate (see e.g., U.S. Patent No. 5,013,765). Based on the chemical structure of the PPSU polymer, it was anticipated that sulfonation of PPSU could be achieved using a sulfuric acid (solvent)/sulfur trioxide (sulfonating agent) system. Our results indicate that controllable sulfonation of PPSU is not possible with a sulfuric acid solvent.

10

Another method was investigated using a combination of DMF/sulfur trioxide. This method also was found to be unsuccessful in producing a sulfonated PPSU polymer.

15

Still another method was investigated using a sulfonation process employing chlorosulfonic acid (solvent)/sulfur trioxide (sulfonating agent). See e.g., U.S. Patent No. 4,413,106. This method was also found to be unacceptable.

20 It was found in the present invention that controllable sulfonation of PPSU homopolymers, copolymers and blends thereof, can be achieved using a methylene chloride (solvent)/ sulfur trioxide (sulfonating agent) system.

One preferred process of the present invention for preparing PPSU based ion-conducting materials is described as follows: the polymer is first dissolved in
25 a suitable solvent, preferably methylene chloride or another non-reactive solvent, e.g., halogenated hydrocarbons or nitrobenzene and the like. The polymer solution is allowed to stir until the polymer precipitates and a slush-like suspension is formed. Sulfonation is performed by admixture of the PPSU polymer suspension and a sulfonating agent, preferably, sulfur trioxide. The

-22-

amount of sulfonating agent added controls the degree of sulfonation. Preferably, temperatures are maintained between -10 to 25°C.

5 The methods for preparing PPSU based ion-conducting materials of the present invention may be further optimized by additional dilution of the polymer solution with solvent and extending the addition time of the sulfonating agent.

10 In accordance with the methods of the present invention, addition of sulfur trioxide to the slush-like suspension did not cause agglomeration during sulfonation. Rather, the reaction product was maintained as a suspension (e.g., a very finely dispersed powder) which was recovered by filtration. The product was then washed with solvent, e.g., methylene chloride, and air dried. Surprisingly, we discovered that use of $\text{CLSO}_3\text{H}/\text{CH}_2\text{Cl}_2$ was not compatible with such a suspension.

15

Generally preferred concentration ranges for the PPSU based ion-conducting materials of the present invention include the following: 5-30wt.%, preferably 10-20wt% (initial polymer solution, before dilution of any excess solvent).

20

This method can be used to produce highly sulfonated polymeric films (IEC of at least about 0.5 meq./g to at least about 4.0 meq./g), with equally high conductivity (IC of at least about 0.01 to about 0.5 S/cm) and minimal polymeric degradation.

25

Some heterogeneity of the sulfonated PPSU based ion-conducting polymers may result from the sulfonation procedure. Heterogeneity may not be severe enough to cause the polymer to precipitate during the sulfonation procedure, but some distribution may exist as the polymer crystallites sulfonate

-23-

from the outside in. That is, some portions of the sulfonated polymer may be so highly sulfonated as to be water soluble (possibly leaching out during fuel cell operation) or otherwise degraded.

5 Various purification methods can be employed to effectively remove overly sulfonated or degraded fractions of these polymers. In a preferred embodiment, the purification procedure involves re-dissolving the ion-conducting polymer in a suitable solvent (e.g., NMP), and re-precipitating it into water or saturated NaCl solution. Re-precipitation of the ion-conducting polymer into
10 saturated salt solution has been shown to result in a high yield of the ion-conducting polymer, while removing polymer that has been excessively sulfonated or degraded.

 Additionally, there are several methods to improve the long term stability
15 (aqueous hydroperoxide radical) of the ion-conducting materials of the present invention.

 For example, the stability of the ion-conducting materials of the present invention may be enhanced by several post-processing steps. These steps include
20 the following: (i) cross-linking the ion-conducting polymer in the H⁺ form to develop sulfone cross-links; (ii) addition of small amounts of antioxidants (insoluble) into the ion-conducting polymer; and (iii) chlorination / bromination of the ion-conducting polymer backbone, thereby reducing degradation sites.

25 Crosslinking methods can provide or enhance peroxide stability. Additionally, various procedures are described in the literature wherein sulfonated polymers can be crosslinked to further enhance the barrier properties of the ion-conducting polymer. See e.g., U.S. Patent No. 5,795,496; Kerres, et al., "New

Ionomers and their Applications in PEM Fuel Cells", ICE, Stuttgart, Germany (1996); and Kerres, et al., *J. Membrane Sci.* 139:211-225 (1998).

For example, U.S. Patent No. 5,795,496 describes a method of
5 crosslinking ion-conducting polymers via the SO₃H groups (sulfonic acid groups)
to form sulfone crosslinks between polymer chains. This method entails
sulfonating the polymer (e.g., PEEK) using concentrated sulfuric acid, casting of a
film, then heating the film to a temperature of 120°C under vacuum. It is the
heating step which causes the crosslinking to occur.

10

Although the enhanced barrier properties provided by crosslinking, the
crosslinking procedure results in decreased ionic conductivity, water adsorption
and swelling of the polymer. However, adjustments can be made to the
crosslinking procedures employed in order to minimize the sacrifice of ionic
15 conductivity.

The use of additives can also provide or enhance peroxide stability of the
PEK and PPSU based ion-conducting materials of the present invention. Polymer
additives can be used as radical scavengers within the ion-conducting component
20 of the ion-conducting material or SPEM. Examples of these include Irganox 1135
(Primary Phenolic Antioxidant, commercially available from Ciba Geigy) and
DTTDP (Di(tridecyl) Thiodipropionate, Secondary Antioxidant, commercially
available from Hampshire).

25

PEK and PPSU based ion-conducting materials of the present invention
may be used to produce SPEMs using standard membrane casting techniques.
Such techniques are well known to the skilled artisan. For example, films can be
made by dissolving the polymer in a suitable solvent and casting onto a glass plate
(or other surface). More specifically, the ion conducting polymer can be dissolved

-25-

in n-methyl pyrrolidone (NMP), filtered, and then cast onto the substrate. The films are slowly evaporated in a low humidity chamber, then dried in a vacuum oven to fully densify. Once dry the films can be removed from the casting substrate by immersion in water.

5

The PEK and PPSU based ion-conducting materials and SPEMs of the present invention have limited methanol permeability (limited methanol diffusivity and solubility) even at elevated temperatures and pressures, are substantially chemically stable to acids and free radicals, and

10 thermally/hydrolytically stable to temperatures of at least about 100°C.

The PEK and PPSU based ion-conducting membranes of the present invention have an ion-exchange capacity (IEC) of >1.0meq/g dry membrane (preferably, 1.5 to 2.0meq/g) and are highly ion-conducting (preferably, from

15 about 0.01 to about 0.5S/cm, more preferably, to greater than about 0.1 S/cm or <10Ωcm resistivity).

Ion-conducting materials and SPEMs of the present invention are durable, substantially defect-free, and dimensionally stable (less than about 20% change in

20 dimension wet to dry), preferably even above temperatures of at least about 100°C.

Particularly preferred PEK and PPSU based ion-conducting materials have the ability to survive operation in fuel cells (i.e., H₂/O₂, methanol) for at least

25 about 5000 hours (e.g., automotive applications).

The PEK and PPSU based ion-conducting materials for use in the present invention may be substituted or unsubstituted. These materials may be present as homopolymers, copolymers, or other blends. The class of PEK and PPSU

homopolymers, copolymers, and blends thereof disclosed herein may include any desired substituents, provided that such substituents do not substantially impair properties desired for the intended use of the polymer, as may readily be determined by one of ordinary skill in the art. Such properties may include ionic conductivity, chemical and structural stability, swelling properties and so forth.

The utility of blending polymers to form a PEK and PPSU based ion-conducting material of the present invention is in optimizing each of their properties. Unlike simple mixing, blending does not create a composite material with two dispersed components. Rather, the blend is uniform in composition throughout. It may be useful to blend a sulfonated polymer with an unsulfonated one to optimize swelling, fuel crossover resistance, conductivity, peroxide resistance, hydrolytic stability and the like. Similarly, the blending of two sulfonated polymers might allow improved properties over each individual component. This concept may also be employed to improve the strength, cost, processability or stability of the ion-conducting materials of the present invention.

Utilizing the innovative PEK and PPSU based ion-conducting materials and membranes of the present invention, relatively low cost ion-conducting materials of the present invention may be produced which exhibit improved power density and reduced sensitivity to carbon monoxide in hydrogen fuel.

Ion-conducting materials of the present invention also alleviate water management problems which limit the efficiency of present Nafion® membrane-based fuel cells.

Ion-conducting materials of the present invention exhibit resistance to degradation and hydrolysis, as well as resistance to stress-induced creep.

-27-

Ion-conducting materials of the present invention exhibit high ionic conductivity, high resistance to dehydration, high mechanical strength, chemical stability during oxidation and hydrolysis, low gas permeability to limit parasitic losses, and stability at elevated temperatures and pressures.

5

Ion-conducting materials of the present invention are resistant to methanol crossover when used in a direct methanol fuel cell. This results in high efficiency and improved cell performance.

10

Ion-conducting materials of the present invention utilize relatively low cost starting materials and fabrication methods, and therefore can be produced at a fraction of the cost of those membranes employing Nafion® and Nafion®-like ionomers.

15

Ion-conducting materials of the present invention of the present invention act as a barrier against reactants (H_2 , O_2 and methanol permeation) in fuel cell applications.

20

Surfactants or surface active agents having a hydrophobic portion and hydrophilic portion may be utilized in producing ion-conducting materials of the present invention of the present invention. These agents are well known in the art and include Triton X-100 (commercially available from Rohm & Haas of Philadelphia, PA).

25

Compatibilizers may also be employed in producing membranes of the present invention. As used herein, "compatibilizers" refer to agents that aid in the blendability of two or more polymers that would otherwise be resistant to such blending. Examples include block copolymers containing connecting segments of each component.

The PEK and PPSU-based ion-conducting materials, SPEMs and methods of the present invention will be further illustrated by the Table and Examples below.

The following table further illustrates the ion-conducting materials and SPEMs of the present invention.

TABLE 1

Serial Number	ICP Type (ID)	ICP (% wt)	Thickness (mils)	Thickness (mils)	Wet	% Dry Vol ICP (Est.)	IEC (meq./g)	Water Content (%)	Conductivity (S/cm)	Resistance (ohm cm ²)	Peroxide Test	1M Me(OH) Perm. @ 60°C (Normalized for Thickness)	Dimensional Stability (% Area Change)
Nafion Control	Nafion 117 (1100EW)	100	Dry 7.1		8.7	100	0.90	38	1.088E-01	0.203	-3.2%	NT	-20%
FMI 026-127A	200% SPPSU (Radel R)	100	1.8		2.1	100	1.67	144	7.307E-02	0.073	NT	81% of Nafion 117	-84%
FMI 026-127B	200% SPPSU (Radel R)	100	1.8		2.8	100	1.90	174	9.118E-02	0.078	NT	138% of Nafion 117	-153%

NT = not tested

-30-

EXAMPLES OF THE INVENTION

Commercial Availability of Starting Materials:

Radel® polyphenyl sulfone polymer is commercially available from Amoco Polymers.

5

Victrix® poly (aryl ether ketone) polymer is commercially available from Victrix USA.

General Procedures:

- 10 The following procedures were employed in the fabrication and testing of samples that were prepared in accordance with the materials, membranes and methods of this invention.

IEC PROCEDURE:

- 15 1. Cut out pieces of sulfonated films (target weight 0.2g, target film thickness 2 mils).
2. Vacuum dry films at 60°C, record dry weights and note if films are in H⁺ or Na⁺ form.
3. Boil deionized water in separate beakers on hotplate.
- 20 4. Place films into boiling water.
5. Boil films vigorously for 1/2 hour.
6. Prepare 1.5N H₂SO₄.
7. Place films into H₂SO₄ and soak for 1/2 hour.
8. Remove films and rinse with deionized water.
-
- 25 9. Boil in deionized water again. Repeat until the films have soaked in H₂SO₄ three times.
10. Remove films from boiling water, pat film surface with paper towel, and rinse carefully with deionized water.
11. Place films in another beaker of water and check for pH.

-31-

12. Continue to rinse the films with water until pH is neutral to remove any excess acid trapped in the folds of the film.
13. Prepare saturated NaCl solution.
14. Boil the NaCl solution, pour into screw cap vials, add film and cap.
- 5 15. Place capped vials with film into water bath at 90°C for 3 hours.
16. Remove capped beaker from water bath and cool to room temperature.
17. Remove the films from NaCl solution by pouring the salt solution into another beaker (save), wash the films with deionized water (save all washings – they will be used for titration).
- 10 18. Titrate the NaCl solution with 0.1N NaOH.
19. Take the films, pat with paper towel and take wet weight. (Use wet weight to determine water content of films.)
20. Dry the films under vacuum at 60°C until constant weight.
21. Take dry weight and use this to calculate IEC.

15

PEROXIDE TEST PROCEDURE:

22. Place films into the H+ form by following steps 1-12.
23. Make peroxide solution by adding 4ppm Fe to 3% hydrogen peroxide (28.5mg of ammonium iron (II) sulfate hexahydrate per liter of peroxide obtained from Aldrich).
- 20 24. Place the peroxide solution into water bath at 68°C.
25. Add films to the peroxide solution already at 68°C.
26. Peroxide test for 8 hours and record film properties (mechanical, color, handling etc.).
- 25 27. If film passes, remove from peroxide, rinse with water to remove all traces of peroxide solution.
28. Follow steps 13-21 to obtain post-peroxide test IEC.

CROSSLINKING PROCEDURES

Ion-conducting polymeric samples can be crosslinked in the acid (H⁺) form to improve ICP stability. Normally, crosslinking is performed in vacuum, to exclude oxygen from the system (which can cause ICP charring). The vacuum oven should be preheated to temperatures of at least about 200°C. The ICP sample is then heated in the vacuum oven for a prolonged period of time. The ICP sample should be tested before and after crosslinking for IEC and peroxide stability in order to evaluate long term membrane stability. See e.g., Example 5 below.

FILM FABRICATION PROCEDURES:

Film Casting.

Ion-conducting materials of the present invention may be used to produce SPEMs using standard membrane casting techniques. Such techniques are well known to the skilled artisan. For example, films can be made by dissolving the polymer in a suitable solvent and casting onto a glass plate (or other surface). More specifically, the ion conducting polymer can be dissolved in n-methyl pyrrolidone (NMP), filtered, and then cast onto the substrate. The films are slowly evaporated in a low humidity chamber, then dried in a vacuum oven to fully densify. Once dry the films can be removed from the casting substrate by immersion in water.

SULFONATION PROCEDURES:

Sulfonation Procedure I:

Aromatic PES polymers can be sulfonated to controlled degrees of substitution with sulfonating agents. The degree of substitution is controlled by the choice of and mole ratio of sulfonating agent to aromatic rings of the polymer, by the reaction temperature and by the time of the reaction. This procedure offers

a method for carrying out sulfonation in a heterogeneous manner, i.e., sulfonation of precipitated polymer crystals.

5 The polymer (preferably a polyethersulfone) is first dissolved in the appropriate solvent (preferably methylene chloride) and then allowed to precipitate into a fine crystalline suspension. Sulfonation is carried out by simple admixture of the suspension with a sulfonating agent. Suitable agents include chorosulfonic acid and, preferably, sulfur trioxide (Allied chemicals stabilized Sulfan B® in CH_2Cl_2). The sulfonating agent used should be in sufficient
10 proportion to introduce a number of sulfonate groups onto the polymer that is within the range of between 0.4:1 to 5:1 per polymer repeat unit, although this is not critical. The temperature at which sulfonation takes place is critical to limiting the side reactions but varies with the type of polymer (a preferable temperature is within the range of from -50° to 80°C , preferably -10° to $+25^\circ\text{C}$).

15

When the desired degree of sulfonation has been reached, the sulfonated polymer may be separated from the reaction mixture by conventional techniques such as by filtration, washing and drying.

20

The polymer products of the process of the invention may be neutralized with the addition of a base, such as sodium bicarbonate, when desired and converted to the alkali salts thereof. The alkali salts of the polymer products of the invention may be used for the same purposes as the parent acid polymers.

25

See e.g., U.S. Patent 4,413,106.

Sulfonation Procedure II:

Concentrated sulfuric acid is used as the solvent in this procedure. The content of the sulfonating agent, sulfur trioxide, is based on the total amount of

-34-

pure (100% anhydrous) sulfuric acid present in the reaction mixture, and is kept to a value of less than 6% by weight throughout the entire sulfonation. The sulfur trioxide may be mixed in dissolved form (oleum, fuming sulfuric acid) with concentrated sulfuric acid. The concentration of the starting sulfuric acid and oleum were determined by measuring their density immediately before use in the reactions.

The temperature of the reaction mixture is kept at less than +30°C throughout the reaction. The sulfonation procedure is stopped with the addition of water to the reaction mixture or by pouring the reaction mixture into water.

More specifically, the polymer is first dried in high vacuum at room temperature to constant weight, then dissolved in concentrated sulfuric acid. Oleum is then added drop-wise over a period of hours with constant cooling below +30°C, and with stirring. When all of the oleum has been added, the reaction mixture is stirred for a further period of hours at the same temperature. The resultant viscous solution is then run into water and the precipitated polymer is filtered off. The polymer is then washed with water until the washings no longer are acidic, and it is then dried.

If these conditions are maintained, a controllable sulfonation of aromatic polyether sulfones is possible and polymer degradation can be substantially or completely prevented.

Though less preferred, another variation of this procedure is to add the sulfur trioxide either in pure solid state or in gaseous state to a solution of the polymer in concentrated sulfuric acid.

See e.g., U.S. Patent 5,013,765.

ION-CONDUCTING MATERIALS - TESTING METHODS

IEC. % Water Content, Membrane Degradation:

During this procedure, films are immersed in distilled H_2O and boiled for a period of 30 minutes. The films are then placed in a solution of 1.5N H_2SO_4 at room temperature and soaked for a period of 30 minutes. This is repeated three separate times to ensure proper H^+ ion exchange into the membrane. Films are rinsed free of acid (pH of rinse water > 5.0) and placed into separate beakers, each filled with a saturated solution of NaCl. The salt solution is boiled for a period of three hours. The films, which are now in the Na^+ form, are removed from the salt solution, rinsed with distilled water and padded to remove excess water. Now a wet weight and thickness of the sample are measured. While in the Na^+ form, the films are dried in an air oven at a temperature of $60^\circ C$. The dry weight and thickness of the films are measured and the percent water content is calculated. The salt solutions are titrated with 0.1N NaOH to a phenolphthalein endpoint and IEC dry (meq/g) values calculated.

Ionic Conductivity:

Transverse ionic conductivity measurements are performed on film samples in order to determine the specific resistance ($ohm \cdot cm^2$). Prior to the ionic conductivity measurements, film samples are exchanged into the H^+ form using the standard procedure discussed above. To measure the ionic conductivity, the film samples are placed in a die consisting of platinum-plated niobium plates. The sample size tested is $25cm^2$. Prior to assembling in the measuring device, platinum black electrodes are placed on each side of the film sample to form a membrane-electrode assembly (MEA). To insure complete contact during the resistivity measurement, the MEA is compressed at 100 to 500 psi between two platinum-plated niobium/stainless steel rams. The resistance of each film is determined at 1000 Hz, 1 to 5A, with a four point probe resistance measuring device and converted to conductivity by using formula 1.

-36-

$$(1) C = t/RxA$$

Where: C = Conductivity (S/cm)

R = Sample Resistance (ohm)

5 t = Wet sample thickness (cm)

A = Sample area (cm²)

Measurements are converted to specific resistance by calculating the ratio of thickness over conductivity (ohm*cm²).

10

Membrane Degradation.

Accelerated degradation testing is carried out using 3% H₂O₂ solution with 4 ppm Fe⁺⁺ added as an accelerator. The films are tested for a period of 8 hours at a temperature of 68°C. The percent degradation of IEC was measured in the film samples after the test. After 8 hours, the films are removed from solution, and re-exchanged using 1.5 N H₂SO₄. The IEC is recalculated, and the test result expressed as the % loss in IEC. This test simulates long term (several thousand hours) of actual fuel cell operation. For H₂O₂, fuel cells, <10% IEC degradation in this test would be considered acceptable.

20

Example 1

Sulfonation of Radel R® Using Sulfan B® (100% and 150% Sulfonation)

Sulfonation Procedure I was used in the following example.

25

Two separate 1000 ml 3 neck resin kettles (with ribs) equipped with an N₂ inlet, addition funnel, and overhead stirrer were charged with the following reactants: 340 ml of dichloromethane and 50.00 grams of Radel R® Polyphenyl Sulfone Polymer (beads). These mixtures were stirred until solutions formed

-37-

(approximately .25 hours). Once solutions formed, they were cooled in ice baths to about a temperature of 0°C (ice bath was maintained throughout the duration of the addition and reaction). (Note that Radel R® was dried at 70°C under full dynamic vacuum for about 12 hours to remove any adsorbed moisture.)

5

While the above solutions were cooling, the following amounts of Sulfan B® were combined with dichloromethane in two separate 125 ml addition funnels. In funnel #1 (100% sulfonation) 10.00 grams of Sulfan B® was combined with 120 ml of dichloromethane. In funnel #2 (150% sulfonation) 15.00 grams of Sulfan B® was combined with 120 ml of dichloromethane.

10

As polymer solutions were cooled, the polymer precipitated from solution to form a viscous paste. To each of these polymers approximately 350 ml of dichloromethane was added to aid in the uniform mixing of the suspensions. The diluted suspensions were then cooled to ice bath temperatures once again.

15

To the rapidly stirring cooled and diluted polymer suspension, the Sulfan B® solutions were added drop-wise over a period of 3.5 to 4.0 hours.

20

Upon completing the addition of the Sulfan B® /dichloromethane solution, the reaction mixtures were permitted to stir at ice bath temperatures for another 2.5 hours, then the reaction was stopped by adding approximately 10 ml of deionized water to each of the reaction mixtures.

25

The reaction mixtures (white dispersions) were recovered by filtration using a glass frit. Products (white powder) were washed 3X with 100 ml portions of dichloromethane. The washed products were then permitted to air dry in the hood. 20% solutions of the dried products were made in NMP and cast on soda lime glass plates. The freshly cast films were left to stand in a dry box with a

-38-

relative humidity of less than 5% for a period of 24 hours. The cast films were heated at 70°C under full dynamic vacuum for an hour prior to floating the films off with deionized water. The floated films were then permitted to air dry overnight.

5

The 100% and 150% sulfonated products swell greatly in water and become opaque, but when films are dry they shrink and become clear once again. The mechanical strength of these films allows creasing while resisting tearing. Films of the 100% and 150% products are not soluble in boiling water, and under these conditions also maintain their mechanical properties.

10

IEC: 100% sulfonated Radel R® unpurified = 1.39 meq./g
150% sulfonated Radel R® unpurified = 1.58 meq./g

15

These polymers were further purified by dissolving in NMP (at 20wt.%) and then precipitated into a large excess of saturated salt water. The resulting polymers were soaked in sodium bicarbonate, washed several times with water, then dried under vacuum (~100°C). These polymers were also cast into films as described above for characterization.

20

IEC: 100% sulfonated Radel R® purified = 1.26 meq./g
150% sulfonated Radel R® purified = 1.44 meq./g

Water Pick-up (wt.%):

25

100% sulfonated Radel R® purified = 56%
150% sulfonated Radel R® purified = 110%

Example 2

Sulfonation of Radel R® Using Sulfan B® at 200% Stoichiometric Sulfonation

Procedure:

5 This sulfonation reaction was run very similarly to those previously described in Example 1 (100, 150% sulfonations with Sulfan B®), with the adjustments noted below:

- 10 - After the precipitation of the polymer from the initial dichloromethane solutions, only 200ml of new solvent was added to enhance stirring (in Example 1, an additional 350ml was used).
- 15 - Previous data suggests that not all of the SO₃ reacts with the polymer over 6 hours at 0-5°C. Therefore, one reaction was carried out at ice bath temperatures for 8 (or more) hours and then allowed to warm to room temperature. Although the resulting sulfonated Radel R® was darker in color than the batch that was quenched after only 6 hours, the polymer was still water insoluble and showed good film properties. The properties of these ICPs were:

20 200% Sulfonated Radel R (quenched after 6 hrs at 0-5°C):
IEC = 1.67 meq/g, Water Pick-up = 144%, Conductivity = 0.073 S/cm

200% Sulfonated Radel R (quenched after allowed to warm up):
IEC = 1.90 meq/g, Water Pick-up = 174%, Conductivity = 0.091 S/cm

25

- A similar reaction was carried out in which the SO₃ was allowed to react longer, but was kept cold (0-5°C) throughout the reaction. The product isolated from this reaction had an IEC value (1.71meq./g) which was between the two batches described above.

Note: Percent sulfonation in terms of stoichiometry, e.g., 200% sulfonation, refers to the use of a particular excess per each polymeric repeat unit, e.g., two moles in the case of 200% sulfonation.

5

Example 3

Sulfonation of Radel R Using Sulfan B at 220% Stoichiometric Sulfonation

Procedure:

- 10 Two sulfonation experiments were run according to Examples 1 and 2 with the adjustments noted below:
- After the precipitation of the polymer from the initial solution, 350ml of dichloromethane was added to aid in stirring.
 - 15 - 22g of Sulfan B was combined with approximately 115ml of dichloromethane (corresponding to 220% sulfonation of the monomer unit). This solution was added drop wise to each polymer suspension (previously chilled in an ice bath) over the course of 4 hours.
 - After addition, the reactions were kept packed in ice for approximately 10
 - 20 hours and then allowed to warm to room temperature.
 - After quenching with a few milliliters of water, each was filtered and then washed with dichloromethane, as well as tetrahydrofuran.
 - The sulfonated polymers were dried overnight, dissolved in NMP (at 20wt.%) and then precipitated into a large excess of distilled water, followed by
 - 25 soaking in sodium bicarbonate solution (to convert to the sodium salt form). After neutralization, the gelatinous polymer precipitate was rinsed several times with deionized water.
 - One reaction (Sample A) was filtered and allowed to dry. The second reaction (Sample B) was added to approximately 4 liters of acetone. The acetone

-41-

caused the collapse of the water swollen polymer which was then isolated by filtration. It also caused a significant portion to dissolve, which was isolated by drying of the acetone / water mixture (Sample B-1). Samples B and B-1 contained approximately the same amount of polymer, but showed varying properties. In particular, the sulfonated polymer that was not extracted into acetone showed a slightly lower IEC, and a significantly lower water up-take.

220% Sulfonated Radel R:

Sample A: IEC = 2.08 meq./g, water pick-up = 306wt.%, IC = 0.179 (S/cm)
Sample B: IEC = 1.82 meq./g, water pick-up = 128wt.%, IC = 0.155 (S/cm)
Sample B-1: IEC = 2.12 meq./g, water pick-up = 432wt.%, IC = 0.132 (S/cm)

Example 4

Sulfonation of Victrex ® Poly(Ether Ketone) Using H_2SO_4 / SO_3

Sulfonation Procedure II was used in the following example.

Procedure:

30.00g PEK polymer was dissolved in 270g of concentrated sulfuric acid (93.5wt.%) under nitrogen, stirred by an overhead mechanical stirrer. The polymer was dispersed over several days to form a dark red thick solution.

176g of this solution was left in the three neck flask with overhead stirrer, N_2 , etc. To the flask, 208.4g of fuming sulfuric acid (25.5wt. % free SO_3) was added over the course of a few minutes with constant stirring to raise the solution to a free SO_3 content of 2wt. %. The resulting solution was immersed in a room temperature water bath to control the temperature.

-42-

Samples were removed after approx. 1 hour, 3 hours, and 16 hours, and quenched into deionized water to precipitate.

In order to make films, the 1 and 3 hour products were washed several
5 times with deionized water, soaked overnight in approximately 0.5M NaOH solution, then washed until a neutral pH was achieved. These were blotted dry and placed in the vacuum oven overnight at 50°C. Dried samples were dissolved in NMP to make a 20wt. % solution. This required heating overnight at 60°C. Films of approx. 6 mils were cast onto a freshly cleaned glass plate. After two
10 days of drying the films were removed by immersion into deionized water.

Soaking the films in water (at room temperature) caused considerable swelling to give a hazy gel-like consistency, but the 1 hour and 3 hour samples did not dissolve. Film of the 1 hour product could be hydrated and dehydrated, while
15 maintaining resistance to tearing. The 1 hour sulfonated PEK film IEC was measured to be 2.3meq/g.

Example 5

Crosslinking of Sulfonated PPSU

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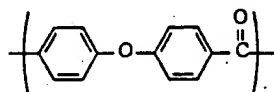
Ion-conducting polymeric samples can be crosslinked in the acid (H⁺) form to improve ICP stability. Normally, crosslinking is performed in vacuum, to exclude oxygen from the system (can cause ICP charring). For example, SPPSU was crosslinked in a vacuum oven preheated to temperatures of 200, 225 and
25 250°C for durations of up to 8 hours. Under these conditions, samples showed a slight IEC loss (~10%), and little improvement in long term stability (peroxide test). More severe conditions were employed by exposing samples to 250°C in full vacuum for more than 20 hours. Peroxide testing did not show any considerable difference between SPPSU crosslinked films and SPPSU controls

- until heated for at least 32 hours. The SPPSU films crosslinked at 250°C for 32 hours and 72 hours maintained their film integrity during the peroxide accelerated life test. The IEC of these test samples decreased significantly. Specifically, a loss of 63% (1.90 to 0.69 meq/g) for the 32 hour sample and a loss of 73% (1.90 meq/g to 0.51 meq/g) for the 72 hour crosslinked SPPSU films was calculated.
- 5 It is anticipated that many of the SO_3H acid groups form aromatic sulfone ($\text{Ar-SO}_2\text{-Ar}$) crosslinks between polymer chains. This trend confirms that crosslinking (H^+ form) of sulfonated polymers can be used to improve long term membrane stability.
-

What is claimed is:

1. An ion-conducting material comprising at least one polyaryletherketone (PEK) homopolymer or at least one PEK copolymer, or blends thereof, wherein the PEK homopolymer, PEK copolymer or blends thereof are sulfonated and the ion-conducting material is devoid of ether-phenyl-ether linkages.

2. The ion-conducting material of claim 1, wherein the PEK homopolymer comprises repeating units of the formula



wherein the phenyl rings may be substituted or unsubstituted.

3. The ion-conducting material of claim 1 having an IEC from at least about 0.5 meq./g to at least about 4 meq./g.

4. The ion-conducting material of claim 1, further comprising sulfone crosslinkages.

5. The ion-conducting material of claim 1, further comprising antioxidants.

6. The ion-conducting material of claim 1, wherein the ion-conducting material is halogenated.

7. The ion-conducting material of claim 6, wherein the ion-conducting material is brominated or chlorinated.

8. A solid polymer electrolyte membrane comprising the ion-conducting material of claim 1.

9. The solid polymer electrolyte membrane of claim 8, wherein the ion-conducting material comprises sulfone crosslinkages.

10. A method of producing an ion-conducting material devoid of ether-phenyl-ether linkages suitable for use in electrochemical applications comprising:
providing a solution of at least one PEK homopolymer, PEK copolymer or blends thereof;

adding a sulfonating agent to the PEK homopolymer, PEK copolymer or blend solution to form a sulfonated PEK homopolymer, PEK copolymer or blend;
and

isolating the sulfonated PEK homopolymer, PEK copolymer or blend thereof from the solution.

11. The method of claim 10, wherein the sulfonating agent comprises at least one of sulfur trioxide, concentrated sulfuric acid and fuming sulfuric acid.

12. The method of claim 11, wherein the sulfonating agent has a free sulfur trioxide content of about 0 (about 100% sulfuric acid) to about 30 wt.% (about 70% sulfuric acid).

13. The method of claim 10, wherein the PEK polymer solution is maintained at a reaction temperature from about 10°C to about 60°C.

14. The method of claim 10, further comprising casting a membrane of the ion-conducting material.

15. The method of claim 10, further comprising crosslinking the ion-conducting material.

16. The method of claim 15, wherein the ion-conducting material is crosslinked in the H⁺ form by a thermal process.

17. The method of claim 10, wherein isolating the sulfonated PEK homopolymer, PEK copolymer or blends thereof, comprises re-precipitating the sulfonated PEK homopolymer, copolymer or blends thereof into water, water saturated with sodium chloride, methanol or other non-solvent.

18. The method of claim 10, further comprising adding antioxidants to the sulfonated PEK homopolymer, PEK copolymer or blends thereof.

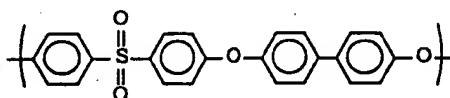
19. The method of claim 18, wherein the antioxidant is introduced following isolation of the sulfonated PEK homopolymer, PEK copolymer or blends thereof.

20. The method of claim 10, further comprising halogenating the aromatic backbone of the sulfonated PEK homopolymer, PEK copolymer or blends thereof.

21. The method of claim 10, further comprising chlorinating or brominating the aromatic backbone of the sulfonated PEK homopolymer, PEK copolymer or blends thereof.

22. An ion-conducting material comprising at least one sulfonated polyphenylsulfone (PPSU) homopolymer, PPSU copolymer or blends thereof.

23. The ion-conducting material of claim 22 having repeating units of the formula



wherein the phenyl rings may be substituted or unsubstituted.

24. The ion-conducting material of claim 22, having an IEC from at least about 0.5 meq./g to about 4 meq./g.

25. The ion-conducting material of claim 22, further comprising sulfone crosslinkages.

26. The ion-conducting material of claim 22, further comprising antioxidants.

27. A solid polymer electrolyte membrane comprising the ion-conducting material of claim 22.

28. The solid polymer electrolyte membrane of claim 27, wherein the ion-conducting material comprises sulfone crosslinkages.

29. A method of producing an ion-conducting material suitable for use in electrochemical applications comprising:

providing a solution of a PPSU homopolymer, PPSU copolymer or blends thereof;

allowing the PPSU homopolymer, PPSU copolymer or blends thereof to precipitate from the solution;

adding a sulfonating agent comprising sulfur trioxide to the solution to form a sulfonated PPSU homopolymer, PPSU copolymer or blends thereof, wherein the sulfur trioxide is diluted in a halogenated hydrocarbon or a nitrobenzene solvent; and

isolating the sulfonated PPSU polymer from the solution.

30. The method of claim 29, wherein the halogenated hydrocarbon solvent comprises methylene chloride.

31. The method of claim 29, further comprising purifying the ion-conducting material to remove overly sulfonated or degraded fractions of the ion-conducting material.

32. The method of claim 31, wherein purifying the ion-conducting material comprises re-dissolving the sulfonated PPSU polymer in a solvent, and re-precipitating the sulfonated PPSU polymer into water, water saturated with sodium chloride, methanol or other non-solvent.

33. The method of claim 29, further comprising casting a membrane of the ion-conducting material.

34. The method of claim 29, further comprising crosslinking the ion-conducting material.

35. The method of claim 34, wherein the ion-conducting material is crosslinked in the H⁺ form by a thermal process.

36. The method of claim 29, further comprising adding an antioxidant to the sulfonated PPSU polymer.

37. The method of claim 29, wherein the antioxidant is introduced following isolation of the sulfonated PPSU polymer.

38. The method of claim 29, further comprising halogenating the ion-conducting material.

39. The method of claim 29, further comprising chlorinating or brominating the ion-conducting material.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/19470

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08G 14/00; C08J 5/20

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 528/125, 128, 175, 226, 229, 373, 391; 525/328.5, 471, 535; 521/27, 28

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN, search terms: (polyaryletherketone or PEK or polyether ketone), electrolyte, ,embrane, sulfonat?, (sulfur trioxide or sulfuric acid)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,438,082 A (HELMER-METZMANN et al.) 01 August 1995, abstract, formulas VII, VIII, col. 2, lines 5 et seq.	1-39
Y	US 5,362,836 A (HELMER-METZMANN et al.) 08 November 1994, abstract, formulas I, VII, VIII, col. 2, lines 14 et seq.	1-39
Y	US 5,561,202 A (HELMER-METZMANN et al.) 01 October 1996, abstract, formulas I, VII, VIII, col. 2, lines 1 et seq.	1-39

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

A	document defining the general state of the art which is not considered to be of particular relevance	*T*	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
B	earlier document published on or after the international filing date	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
L	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
O	document referring to an oral disclosure, use, exhibition or other means	*A*	document member of the same patent family
P	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

24 FEBRUARY 2000

Date of mailing of the international search report

02 MAR 2000

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER:

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